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(54) [Title of the invention]
HEAT-SENSITIVE RECORDING SHEET

(57) [Abstract]
[Object] To provide a heat-sensitive recording sheet which is excellent in image quality, glossiness and image clarity as well as in recording characteristics.
[Constitution] A heat-sensitive recording sheet comprising a substrate, a heat-sensitive coloring layer provided on at least one side of the substrate, an intermediate layer optionally provided on the heat-sensitive coloring layer, and a gloss layer formed on the heat-sensitive coloring layer or the intermediate layer, the gloss layer being composed of an outer coating layer containing a white pigment and an unsaturated organic compound curable by irradiation with an electron beam and an inner coating layer containing as a main component an unsaturated organic compound curable by irradiation with an electron beam, the outer coating layer being formed by being released from a shaping surface with high smoothness, characterized in that the outer coating layer comprises at least one non-reactive lubricant selected from the group consisting of alkyl phosphates wherein the alkyl has at least 14 carbon atoms and salts thereof.
[Effects] The heat-sensitive recording sheet of the present invention is excellent in image quality, glossiness and image clarity as well as in recording characteristics.

[Claims]

[Claim 1] A heat-sensitive recording sheet comprising a substrate, a heat-sensitive coloring layer provided on at least one side of the substrate, an intermediate layer optionally provided on the heat-sensitive coloring layer, and a gloss layer formed on the heat-sensitive coloring layer or the intermediate layer, the gloss layer being composed of an outer coating layer containing a white pigment and an unsaturated organic compound curable by irradiation with an electron beam and an inner coating layer containing as a main component an unsaturated organic compound curable by irradiation with an electron beam, the outer coating layer being formed by being released from a shaping surface with high smoothness, characterized in that the outer coating layer comprises at least one non-reactive lubricant selected from the group consisting of alkyl phosphates wherein the alkyl has at least 14 carbon atoms and salts thereof.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application]

The present invention relates to a heat-sensitive recording sheet, more specifically to a heat-sensitive recording sheet which provides recorded images that are excellent in image quality, glossiness and image

clarity, as well as excellent recording characteristics.

[0002]

[Prior Art]

Heat-sensitive recording sheets generally comprise a support made of paper, synthetic paper, plastic film or the like, and a heat-sensitive coloring layer formed on one side of the support and containing as main constituents a colorless or pale-colored coloring substance such as electron-donating leuco dye, an organic acidic developer such as an electron-accepting phenol compound, and a binder. The color-forming dye is reacted with the developer upon application of thermal energy to thereby form a colored recorded image. Such recording sheets have advantages in that recording devices used therefor are compact, inexpensive and easy to maintain, and thus are in extensive use not only as recording media for facsimile machines, ticket-vending machines, scientific measuring instruments and so on, but also as output media in printers or plotters for POS labels, CAD, CRT medical images or the like.

[0003]

Among them, for use in image printers in CRT medical measuring instruments which require uniformity and high resolution in recorded images and for use in CAD plotters which require dimensional stability and fine-line

recording, synthetic paper of multi-layer structure and biaxially oriented thermoplastic resin films optionally containing an inorganic pigment are used. For high value-added heat-sensitive recording sheets, such as video printer paper, not only high image quality, but also enhanced glossiness and image clarity are demanded. However, in order to achieve enhanced glossiness and image clarity as well as excellent quality in recorded images, such as high uniformity and resolution, it is necessary to improve the texture and cushioning characteristics of the substrate and additionally to impart high smoothness to the outermost layer of the heat-sensitive recording sheet.

[0004]

One known method disclosed in Japanese Unexamined Patent Publication No. 1987-279980 is to use a coating composition that is curable with an ultra-violet beam or an electron beam in order to impart high smoothness to the outermost layer of a heat-sensitive recording sheet. While this method gave high glossiness, it generated rippling on the surface due to shrinking during curing, thus interfering with image clarity, and resulting in unsatisfactory quality. The present inventors conducted extensive research to overcome the above-noted problem and formerly filed Japanese Patent Application No. 1993-202039 based on the finding that a

gloss layer which is absolutely free of rippling due to shrinking during curing can be produced either by applying onto a substrate heat-sensitive coloring layer, or onto an intermediate layer when such an intermediate layer is provided on the heat-sensitive coloring layer, a coating composition comprising as the main component an unsaturated organic compound curable by irradiation with an electron beam, bringing the resulting coating into close contact with a shaping surface having high smoothness, curing the coating with an electron beam, and then releasing the resulting layer from the shaping surface to thereby transfer the high smoothness of the shaping surface to the gloss layer cured by the electron beam; or by applying the coating composition onto the shaping surface, laminating the resulting coating with a substrate heat-sensitive coloring layer, or with an intermediate layer when such an intermediate layer is provided on the heat-sensitive coloring layer, curing the coating with an electron beam, and then releasing the resulting layer from the shaping surface to thereby transfer the high smoothness of the shaping surface to the gloss layer cured by the electron beam. The above processes enabled the production of a heat-sensitive recording sheet with excellent glossiness and image clarity.

[0005]

However, technical problems were pointed out regarding the above method, that is, the high smoothness imparted to the outermost layer of the heat-sensitive recording sheet increases the contact area between a thermal recording head and the outermost layer, so that the thermal recording head leaves its running trace on the outermost layer or grinds the outermost layer, producing grinding debris which will adhere to the thermal recording head, thereby greatly obstructing proper recording and, additionally, the increased likelihood of the head becoming adhered to the outermost layer under high humidity conditions leads to improper advance of the recording sheet. Hence, the quality of the obtained heat-sensitive recording sheet was not of a satisfactory level.

[0006]

The present inventors formerly filed, as a solution to the foregoing problem, Japanese Patent Application No. 1993-291552 based on the finding of a method wherein a gloss layer is composed of an outer coating layer comprising a specific amount of a white pigment and an unsaturated organic compound curable by irradiation with an electron beam and an inner coating layer mainly comprising an unsaturated organic compound curable by irradiation with an electron beam, and wherein

the outer coating layer is formed by being released from a shaping surface having high smoothness. While this method realized enhanced hardness and toughness of the cured coating film by containing in the outer coating layer a specific amount of the white pigment and unsaturated organic compound curable by irradiation with an electron beam as described above, the method was still unsatisfactory in terms of avoiding recording problems and improper advance of the recording sheet under higher humidity conditions (at a temperature of 30°C and RH of 85% or higher), thus remained to be improved.

[0007]

[Problems to Be Solved by the Invention]

An object of the present invention is to solve the aforementioned problems associated with the prior art heat-sensitive recording sheets and provide a heat-sensitive recording sheet which is excellent in glossiness and image clarity as well as in image quality and recording characteristics under various environmental conditions ranging from low humidity to high humidity.

[0008]

[Means for Solving the Problems]

The present inventors conducted intensive research to achieve the above object and, as a result, developed the present invention.

[0009]

The present invention provides a heat-sensitive recording sheet comprising a substrate, a heat-sensitive coloring layer provided on at least one side of the substrate, an intermediate layer optionally provided on the heat-sensitive coloring layer, and a gloss layer formed on the heat-sensitive coloring layer or the intermediate layer, the gloss layer being composed of an outer coating layer containing a white pigment and an unsaturated organic compound curable by irradiation with an electron beam and an inner coating layer containing as a main component an unsaturated organic compound curable by irradiation with an electron beam, the outer coating layer being formed by being released from a shaping surface with high smoothness, characterized in that the outer coating layer comprises at least one non-reactive lubricant selected from the group consisting of alkyl phosphates wherein the alkyl has at least 14 carbon atoms and salts thereof.

[0010]

Examples of the substrate to be used in the present invention include synthetic paper prepared by heating and kneading a polyolefin resin and a white inorganic pigment, extruding the melt from a die, stretching the extrudate in the longitudinal direction,

laminating one or two layers of a film formed from a polyolefin resin and a white inorganic pigment on both sides of the longitudinally stretched film, and stretching the obtained laminated film in the transverse direction to make the film translucent or opaque. Further examples include a film formed by heating and kneading polyethylene, polypropylene, an ethylene-vinyl acetate copolymer resin, polyvinyl chloride, polystyrene, polyester or like thermoplastic resin either singly or in combination, extruding the melt from a die and biaxially stretching the extrudate; an opaque film formed from a mixture of the above-exemplified resin and a white inorganic pigment by biaxial stretching; and a paper made of pulp fibers such as wood-free paper, mechanical paper, roll paper, recycled paper, coated paper and the like. A support made of pulp fibers, when used, is preferably provided thereon with a coating layer before being provided with a heat-sensitive layer in order to improve the uniformity of the images.

[0011]

The heat-sensitive coloring layer according to the present invention can be formed by applying a heat-sensitive coloring layer coating composition which mainly comprises a colorless or pale-colored electron-donating leuco dye, an organic acidic substance that causes the leuco dye to develop a color by application of heat, and a

binder, and which optionally comprises a cross-linking agent, a pigment, or a thermoplastic substance. It is generally preferred, from the viewpoint of coloring sensitivity and color density, that the coating amount of the heat-sensitive coloring layer be 3 to 15 g/m^2. The coating may be performed using a technique generally employed by those skilled in the art, such as air knife coating, Meyer bar coating, blade coating, reverse roll coating or slit die coating. The surface of the heat-sensitive coloring layer may be subjected to a smoothing treatment, for example, with a super calender, gloss calender, machine calender or the like, in order to improve the coatability and thereby enhance the recording density and sensitivity.

[0012]

As the color-forming dye, a colorless or pale-colored electron-donating leuco dye that reacts with the developer upon heating to develop a color is used. The color-forming dye usable in the present invention includes, for example, at least one member selected from the group consisting of 2,2 bis{4-[6'-(N-cyclohexyl-N-methylamino)-3'-methylspiro(phthalide-3,9'-xanthene)-2'-ylamide]phenyl}propane, 3-diethylamino-6 methyl-7-anilinofluoran, 3-piperidino-6-methyl-7-anilinofluoran, 3-(N-methyl-N-cyclohexyl)amino-6-methyl-7-anilinofluoran, 3-

dimethylamino-7-chloroanilinofluoran, 3-[N-ethyl-N-(p-methylphenyl)amino]-6-methyl-7-anilinofluoran, 3-diethylamino-7-(metatrifluoromethyl)anilinofluoran, 3-(N-ethyl-N-tetrahydrofurfuryl)amino-6-methyl-7-anilinofluoran, 3-(N-ethyl-N-isopentyl)amino-6-methyl-7-anilinofluoran, 3-(N,N dibutyl)amino-6-methyl-7-anilinofluoran and like fluoran-based dyes.

[0013]

The developer used in the present invention comprises an electron-accepting organic acidic substance that reacts with the color-forming dye upon heating to thereby develop a color. The developer is liquefied or evaporated at room temperature or higher, preferably 70°C or higher, so that it can react with the color-forming dye, thereby causing the dye to develop a color. The developer is generally used in an amount of 1 to 5 weight parts, preferably 1.5 to 3 weight parts, per weight part of the color-forming dye in order to maximize the color density.

[0014]

The developer includes, for example, at least one member selected from the group consisting of 4,4'-isopropylidenediphenol(bisphenol A), 4,4'-isopropylidenebis(2-chlorophenol), 4,4'-isopropylidenebis(2-methylphenol), 4,4'-isopropylidenebis(2,6-t-butylphenol), 4,4'-sec-

butylidenediphenol, 4,4'-cyclohexylidenediphenol, 4-t-butylphenol, 4-phenylphenol, 4-hydroxydiphenoxide, 4,4'-dihydroxydiphenylsulfone, 2,4'-dihydroxydiphenylsulfone, 3,3'-dihydroxydiphenylsulfone, 3,3'-diamino-4,4'-dihydroxydiphenylsulfone, 3,3'-diallyl-4,4'-dihydroxydiphenylsulfone, 3,3'-dichloro-4,4'-dihydroxydiphenylsulfone, 4-hydroxydiphenylsulfone, 4-hydroxy-4'-isopropyloxydiphenylsulfone, 4-hydroxy-4'-benzyloxydiphenylsulfone, 2,4-dihydroxydiphenylsulfone, 2,4-dihydroxy-4'-methyldiphenylsulfone and 3,4-dihydroxyphenyl-p-tolylsulfone.

[0015]

According to the present invention, the heat-sensitive coloring layer may contain either a water-soluble resin or a water-dispersible resin as the binder. Examples are water-soluble resins such as polyvinyl alcohol, starch, modified starch, gum arabic, gelatin, casein, chitosan, methyl cellulose, hydroxy methycellulose, hydroxy ethylcellulose, polyvinyl pyrrolidone, polyacrylic acid salt, polyacrylamide, polyester resins, styrene-acrylate copolymer resins, styrene-maleic anhydride copolymer resins, methylvinylether-maleic anhydride copolymer resins and isopropylene-maleic anhydride copolymer resins, and water-dispersible resins such as vinyl acetate emulsion, acrylate copolymer emulsion,

methacrylate copolymer emulsion, polyurethane emulsion, polyvinyl chloride emulsion, SBR latex, MBR latex and like emulsions having a good film-forming ability, i.e., a minimum film-forming temperature of 20°C or lower. These resins can be used singly or in combination.

[0016]

It is, however, important to assure that the mixture, which is obtained by mixing the binder with a dispersion of each of the color-forming dye and the developer, does not develop a color, coagulate or exhibit high viscosity, and that the formed heat-sensitive recording layer film is tough and free from desensitization. Preferably, the binder is contained in the heat-sensitive coloring layer in an amount of 8 to 20% by weight based on the weight of the solids of the heat-sensitive coloring layer. An amount of less than 8% by weight decreases the strength of the coating film, while an amount of more than 20% by weight deteriorates the sensitivity.

[0017]

The heat-sensitive coloring layer may also contain a cross-linking agent for curing resins for the purpose of increasing its water resistance. Examples of the cross-linking agent include glyoxal, dialdehyde starch and like dialdehyde compounds, polyethyleneimine and like

polyamine compounds, epoxy compounds, polyamide resins, melamine resins, glyceringlycidylether and like diglycidyl compounds, dimethylolurea compounds, aziridine compounds, block isocyanate compounds, ammonium persulfate, ferric chloride, magnesium chloride, sodium tetraborate, potassium tetraborate and like inorganic compounds, boric acid, boric acid triesters, boron-based polymers, etc. The cross-linking agent may be used in an amount of 1 to 10% by weight based on the weight of the solids of the heat-sensitive coloring layer.

[0018]

The heat-sensitive coloring layer may further contain, in order to increase its whiteness and improve the uniformity of the images, a finely powdered pigment which has high whiteness and an average particle size of 5 μm or smaller. Examples of such pigments include inorganic pigments such as calcium carbonate, magnesium carbonate, kaolin, clay, talc, calcined clay, silica, diatomaceous earth, synthetic aluminum silicate, zinc oxide, titanium oxide, aluminum hydroxide, barium sulfate and surface-treated calcium carbonate and silica; and organic pigments such as urea-formalin resins, styrene-methacrylic acid copolymer resins and polystyrene resins. Preferably, the pigment is contained in an amount of 40% by weight or less based on the weight of the solids of the

heat-sensitive coloring layer so as to prevent a reduction in color density.

[0019]

Examples of usable thermoplastic substances include stearic acid amide, stearic acid bisamide, oleamide, palmitic acid amide, cocamide, behenamide and like fatty acid amides, zinc stearate, calcium stearate, polyethylene wax, carnauba wax, paraffin wax, ester wax and like waxes (or lubricants), dimethyl terephthalate, dibutyl terephthalate, dibenzyl terephthalate, dibutyl isophthalate, phenyl 1-hydroxynaphthoate, 1,2-di(3-methylphenoxy)ethane, 1,2 diphenoxyethane, 1-phenoxy-2-(4-methylphenoxy)ethane, diphenyl carbonate, p-benzylbiphenyl, 2,2'-methylenebis(4-methyl-6-t-butylphenol), 4,4'-butylidenebis(6-t-butyl-3-methylphenol), 1,1,3 tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 2,2'-methylenebis(4-ethyl-6-t-butylphenol), 2,4-di-t-butyl-3-methylphenol, 4,4'-thiobis(3-methyl-6-t-butylphenol) and like hindered phenols, 2-(2'-hydroxy-5'-methylphenyl)-benzotoriazole, 2-hydroxy-4-benzyloxybenzophenone and like sensitizers, antioxidants and UV absorbers.

[0020]

Generally, it is preferred that the thermoplastic substance be contained in the heat-sensitive

coloring layer in an amount of 4 weight parts or less per weight part of the developer. For the purpose of improving the wetting property of the heat-sensitive coloring layer coating composition and preventing fish eyes in the coating, it is possible to further add a wetting property improver such as acetylene glycol or dialkyl sulfosuccinate, a dispersing agent for pigment, a defoaming agent, a fluorescent dye, a coloring pigment and the like.

[0021]

In the heat-sensitive recording sheet of the present invention, it is effective to provide an intermediate layer between the heat-sensitive coloring layer and the gloss layer from the standpoint of ensuring adhesion between the heat-sensitive coloring layer and the gloss layer, preventing the fogging which is apt to occur during the application or curing of the gloss layer, etc. The intermediate layer can be formed by applying, onto the heat-sensitive coloring layer, a coating composition comprising as main constituents a water-soluble and/or a water-dispersible resin, a pigment, a lubricant and a cross-linking agent such that the coating amount after drying is 1.0 to 5.0 g/m^2. A coating amount of less than 1.0 g/m^2 results in a coating film unevenly formed and having pinholes and defects, thus leading to degraded

image quality and surface characteristics. On the other hand, a coating amount exceeding 5.0 g/m^2 results in decreased sensitivity and therefore lowered recording density. The coating may be performed by the same method as that employed for the formation of the heat-sensitive coloring layer.

[0022]

In order to facilitate the formation of the gloss layer and to thereby improve the recording density, sensitivity and glossiness, the surface of the intermediate layer may be subjected to a smoothing treatment with a super calender, gloss calender, machine calender or the like. The amount of the resin to be contained in the intermediate layer is preferably 20 to 80% by weight based on the weight of the solids of the intermediate layer. The amount of the pigment to be contained in the intermediate layer is 20 to 80% by weight based on the weight of the solids of the intermediate layer. If the resin is contained in an amount of more than 80% by weight, sticking may be caused during recording. If the resin is contained in an amount of less than 20% by weight, the barrier property of the coating film is degraded, thereby causing fogging and, additionally, the ability to prevent penetration of the inner coating layer coating composition is decreased,

ultimately failing to strengthen the adhesion between the heat-sensitive coloring layer and the gloss layer.

[0023]

The inner coating layer, which forms a part of the gloss layer of the invention, can be formed by applying a coating composition comprising as a main component an unsaturated organic compound curable by irradiation with an electron beam such that the coating amount after drying is 1.0 to 10.0 g/m^2. If the coating amount is more than 10.0 g/m^2, the sensitivity is deteriorated and, even with the help of an increased coating amount of the heat-sensitive coloring layer, the recording density is decreased. If the coating amount is less than 1.0 g/m^2, the outer coating layer containing a large amount of white pigment cannot be satisfactorily released from the shaping surface and, further, the adhesion of the inner coating layer to the heat-sensitive coloring layer or the intermediate layer is not sufficient.

[0024]

Examples of the electron beam-curable unsaturated organic compound to be used in the inner coating layer forming a part of the gloss layer of the invention include N-vinylpyrrolidone, acrylonitrile or derivatives thereof, styrene or derivatives thereof, acrylamide and like amide group-containing monomers;

benzyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, tetrahydrofurfuryl acrylate, phenoxyethyl acrylate, nonylphenoxyethyl acrylate, acrylates of ε-caprolactone adducts, butoxyethyl (meth)acrylate, 2-hydroxy-3-phenoxypropyl acrylate, cyclohexyl (meth)acrylate, N,N-dimethylamino (meth)acrylate, N,N-dimethylaminoethyl (meth)acrylate, 3-phenoxypropyl acrylate, 2-methoxyethyl (meth)acrylate, polyoxyethylene-epichlorohydrin-modified bisphenol A diacrylate, dicyclohexyl acrylate, epichlorohydrin-modified polyethylene glycol diacrylate, 1,6-hexanediol diacrylate, hydroxypivalate neopentyl glycol diacrylate, nonylphenoxypolyethylene glycol acrylate, ethylene oxide-modified phenoxidized phosphoric acid acrylate, polybutadiene acrylate, caprolactone-modified tetrahydrofurfuryl acrylate, tris(acryloxyethyl) isocyanate, trimethylolpropane triacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol hexaacrylate, polyethylene glycol diacrylate, 1,4-butadienedioldiacrylate, neopentyl glycol diacrylate, and neopentylglycol-modified trimethylolpropane diacrylate. These compounds can be used either singly or in a combination of two or more species.

[0025]

The inner coating layer, which forms a part of the gloss layer of the invention, may contain a finely powdered pigment which has high whiteness and an average particle size of 5 μm or smaller in order to increase its hardness and whiteness and to decrease recording problems and improper advance of the recording sheet. Examples of such pigments include inorganic pigments such as calcium carbonate, magnesium carbonate, kaolin, clay, talc, calcined clay, silica, diatomaceous earth, synthetic aluminum silicate, zinc oxide, titanium oxide, aluminum hydroxide, barium sulfate and surface-treated calcium carbonate and silica; and organic pigments such as urea-formalin resins, styrene-methacrylic acid copolymer resins and polystyrene resins.

[0026]

The above white pigment can be dispersed in the electron beam-curable unsaturated organic compound with the use of a three roll mill, two roll mill, Cowles Dissolver, homomixer, sand grinder, paint conditioner, ultrasonic dispersing machine or the like. The inner coating layer coating composition can be applied using a technique generally employed by those skilled in the art, such as offset gravure coating, air knife coating, Meyer bar coating, blade coating, reverse roll coating or slit die coating.

[0027]

The outer coating layer, which forms a part of the gloss layer of the invention, may be formed by applying a coating composition which comprises at least one non-reactive lubricant selected from the group consisting of alkyl phosphates wherein the alkyl has at least 14 carbon atoms and salts thereof and which further comprises a white pigment (A) and an electron beam-curable unsaturated organic compound (B) in such proportions that the weight ratio (A/B) is 40/60 to 95/5, in such a manner that the coating amount after drying is 1.0 to 10.0 g/m^2. If the coating amount is more than 10.0 g/m^2, the sensitivity is deteriorated and, even with the help of an increased coating amount of the heat-sensitive coloring layer, the recording density is decreased. If the coating amount is less than 1.0 g/m^2, the releasability from the shaping surface after curing is degraded and, further, high image clarity and glossiness are not likely to be achieved.

[0028]

Preferably, the lubricant is contained in an amount of 1 to 10 weight parts per 100 weight parts of the sum of A and B. An amount of less than 1 weight part leads to improper advance of the recording sheet under higher humidity conditions, whereas an amount of more than

10 weight parts decreases the curability of the coating film. Furthermore, a lubricant having an alkyl group with less than 14 carbon atoms has no effect in preventing improper advance of the recording sheet under higher humidity conditions even if it is contained in an increased amount. Examples of usable salts include sodium, potassium and like alkali metal salts, primary amine, secondary amine, tertiary amine and like amine salts having 1 to 20 carbon atoms. It is preferred that the white pigment be contained in an amount as large as possible from the standpoint of enhancing the hardness of the cured coating film. More preferably, the proportion of the white pigment is selected such that the weight ratio A/B is 95/5 or less for achieving high releasability from the shaping surface and providing excellent surface characteristics in the cured coating film, or such that the weight ratio A/B is 40/60 or more for bringing about the desired hardness.

[0029]

The white pigment to be used in the coating composition for the outer coating layer forming a part of the gloss layer of the invention can be suitably selected from the variety of those used for the inner coating layer coating composition. As the electron beam-curable unsaturated organic compound to be contained in the outer

coating layer forming a part of the gloss layer of the invention, acrylate or methacrylate monomers or oligomers having at least one ethylenically unsaturated bond may be used either singly or in a combination of two or more species. It is preferred that the main component be selected from the oligomers so as to provide the desired toughness.

[0030]

Examples of acrylate or methacrylate oligomers having at least one ethylenically unsaturated bond include, for example, urethane acrylate oligomers, polyester acrylate oligomers and butadiene-modified acrylate oligomers. These oligomers can be used singly or in a combination of two or more species. When the coating composition, which is obtained by dispersing a white pigment in the ethylenically-unsaturated-bond-containing monomer or oligomer described above, has high viscosity, it is effective that the coating composition be either diluted with an organic solvent, then applied and dried, or that it be emulsified for increased operability or diluted with water (if it is water-soluble), then applied and dried, and finally cured with an electron beam.

[0031]

The electron beam-curable composition according to the invention may incorporate a polymer that is soluble

therein. However, the use of the polymer in an excessively large amount impairs the curability of the coating film and is not preferable from the standpoint of resistance to scratches, resistance to organic solvents, etc.

[0032]

Examples of other non-reactive lubricants include zinc stearate, calcium stearate, polyethylene wax, carnauba wax, paraffin wax, ester wax and like waxes, lauryl sulfonate, oleyl sulfonate, stearyl sulfonate and like alkyl sulfonates and alkali metal salts or amine salts, glyceryl monomyristate, glyceryl monostearate, glyceryl monooleate, glyceryl distearate, glyceryl dioleate and like glycerine fatty acid esters, diglyceryl monolaurate, diglyceryl dilaurate, tetraglyceryl monolaurate, hexaglyceryl monolaurate, decaglyceryl monolaurate and like polyglycerine fatty acid esters, dimethylpolysiloxane, and their modified products. From the above lubricants, those which do not cause desensitization, decoloring or fogging may be selected and used in a small amount insofar as they do not cause deterioration in curability.

[0033]

The outer coating layer and the inner coating layer are brought into close contact with each other to

thereby form an electron beam-curable gloss layer of the invention, and then cured and unified by irradiation with an electron beam in accordance with either of the following two methods. One method comprises bringing the outer coating layer provided on the highly smooth shaping surface into close contact with the inner coating layer provided on the heat-sensitive coloring layer or the intermediate layer, and irradiating the resulting laminate with an electron beam from the opposite side of the heat-sensitive recording sheet or from the shaping surface side. The other method comprises directly applying the inner coating layer coating composition onto the outer coating layer provided on the highly smooth shaping surface, bringing the obtained layer into close contact with the heat-sensitive coloring layer or the intermediate layer, and irradiating the resulting laminate with an electron beam from the opposite side of the heat-sensitive recording sheet or from the shaping surface side. The latter method may be performed in a similar way to that of the former method if the inner coating layer coating composition is high in viscosity and therefore less likely to penetrate into the outer coating layer coating composition.

[0034]

The surface of the gloss layer formed as

described above exhibits high smoothness, excellent glossiness and image clarity. Specifically, it is preferred that the glossiness be 80% or higher when measured at an angle of 75 degrees in accordance with JIS-Z-8714, and that the image clarity be 80% or higher, preferably 90%, when converted from the value of distinctness of image measured at an optical comb width of 2 mm in accordance with JIS-K-7105.

[0035]

[EXAMPLES]

The present invention will be described below in further detail with reference to the following examples to which, however, the invention is not limited. The parts and percentages used in the examples are all by weight unless otherwise specified.

[0036]

Example 1

A heat-sensitive coloring layer coating composition obtained as described later was applied to one surface of commercially available synthetic paper (trade name "YUPO FPG-80", product of YUPO Corporation) in an amount of 5.5 g/m^2 on a dry weight basis by a bar coating method, and thereon was applied an intermediate layer coating composition in an amount of 1.5 g/m^2 on a dry weight basis. To the resultant intermediate layer, an

inner coating layer coating composition for gloss layer was applied in an amount of 3.0 g/m^2, thereby forming an inner coating layer. Aside from the above, an outer coating layer coating composition was applied to a 75-μm-wide PET film (trade name "Lumirror T", product of TORAY Industries, Inc.) in an amount of 3.0 g/m^2 on a dry weight basis, thereby forming an outer coating layer. Subsequently, the outer coating layer was brought into close contact with the inner coating layer to form a gloss layer composed of the outer coating layer and the inner coating layer, which was then cured by irradiation with an electron beam from the PET film side at an absorbed dose of 3.0 Mrads and an accelerating voltage of 175 kV with an electron-curtain type electron beam accelerator (product of Energy Sciences, Inc.), thereby completely unifying the outer coating layer with the inner coating layer. Thereafter, the PET film was separated from the gloss layer, whereby a heat sensitive recording sheet was obtained.

[0037]

• Preparation of heat-sensitive coloring layer coating composition

Dispersion A (heat-sensitive color-forming dye dispersion)

3-(N,N-dibutyl)amino-6-methyl-7-anilinofluoran	20 parts

10% aqueous solution of polyvinyl alcohol	20 parts
Water	10 parts

Dispersion B (developer dispersion)

4-hydroxy-4'-isopropyloxydiphenylsulfone	50 parts
10% aqueous solution of polyvinyl alcohol	50 parts
Water	25 parts

Each of Dispersions A and B were separately dispersed and pulverized to an average particle size of 1.0±0.3 μm with an Ultra Visco Mill. Thereafter, 30 parts of Dispersion A, 90 parts of Dispersion B, 52 parts of a 60% slurry of calcium carbonate, 40 parts of a 10% aqueous solution of polyvinyl alcohol, 28 parts of a SBR latex (trade name "L-1537", solid conc. 50%, product of Asahi Chemical Industry Co., Ltd.), 11 parts of stearic acid amide (trade name "Cerozol A-877", solid conc. 26.5%, product of Chukyo Yushi Co., Ltd.) and 82 parts of water were mixed to thereby obtain a heat-sensitive coloring layer coating composition.

[0038]

• Intermediate layer coating composition (solid conc. 15%)

An intermediate layer coating composition was prepared by mixing the following:

60% dispersion of kaolinitic clay (with an average particle size of 0.6 μm)	42 parts
Aqueous solution of carboxylic acid-	

modified polyvinyl alcohol (solid conc. 10%) (trade name "Gohsenal T-330", product of The Nippon Synthetic Chemical Industry Co., Ltd.)	200 parts
Acrylic emulsion (trade name "SC-2250", solid conc. 40%, product of Nippon Shokubai Co., Ltd.)	100 parts
Solution of dimethylolurea (trade name "J-001", solid conc. 30%, product of Showa Denko K.K.)	33 parts
40% dispersion of zinc stearate (with an average particle size of 0.9 μm) (trade name "Hymicron F-930", product of Chukyo Yushi Co., Ltd.)	13 parts
Water	279 parts

[0039]

• Outer coating layer coating composition for gloss layer

An outer coating layer coating composition for gloss layer was prepared by mixing the following:

No. 1 fraction kaolin (trade name "UW-90", product of Engelhard Corporation)	65 parts
Urethane acrylate emulsion (trade name "UE-7130", solid conc. 47%, product of Toagosei Co., Ltd.)	70 parts
Potassium myristyl phosphate	2 parts

Water 52 parts

[0040]

• Inner coating layer coating composition for gloss layer

An inner coating layer coating composition for gloss layer was prepared by mixing the following:

Urethane acrylate oligomer
(trade name "BS550", product of
Arakawa Chemical Industries, Ltd.) 70 parts

Trimethylolpropane triacrylate 30 parts

In addition, before forming a gloss layer, a back layer coating composition was applied to the opposite side of the substrate in an amount of 1.5 g/m^2 on a dry weight basis by a bar coating method, after which the obtained coating was subjected to a smoothing treatment with a super calender.

[0041]

• Back layer coating composition

A back layer coating composition was prepared by mixing the following:

Sodium polystyrene solfonate (solid conc. 33%)
(trade name "CHEMISTAT SA-9",
product of Sanyo Chemical Industries, Ltd.) 30 parts

SBR latex (solid conc. 50%)
(trade name "0528",
product of JSR Corporation) 70 parts

10% aqueous solution of oxidized starch (trade name "ACE A", product of Oji Cornstarch Co., Ltd.)	150 parts
60% slurry of kaolinitic clay	67 parts
Water	83 parts

[0042]

Example 2

A heat-sensitive recording sheet was obtained in the same manner as in Example 1 except that, in place of potassium myristyl phosphate, potassium cetyl phosphate of the same amount was used in the preparation of an outer layer coating composition for gloss layer.

Example 3

A heat-sensitive recording sheet was obtained in the same manner as in Example 1 except that, in place of potassium myristyl phosphate, potassium stearyl phosphate of the same amount was used in the preparation of an outer layer coating composition for gloss layer.

Example 4

A heat-sensitive recording sheet was obtained in the same manner as in Example 1 except that the outer coating layer coating composition for gloss layer was replaced with the one prepared by mixing the following:

Calcium carbonate (trade name "Raiton A",

product of Bihokufunka Kogyo K.K.) 67 parts
Urethane acrylate oligomer
(trade name "EB294",
product of Daicel-UCB Co., Ltd.) 30 parts
Myristyl phosphate 2 parts
Toluene 90 parts

[0043]

Example 5

A heat-sensitive recording sheet was obtained in the same manner as in Example 1 except that the outer coating layer coating composition for gloss layer was replaced with the one prepared by mixing the following:

No. 1 fraction kaolin (trade name "UW-90",
product of Engelhard Corporation) 64 parts
Urethane acrylate emulsion
(trade name "WE-301", solid conc. 40%,
product of Dai-ichi Kogyo Seiyaku Co., Ltd.) 80 parts
Potassium stearyl phosphate 2 parts
Polysiloxane
(solid conc. 33%, product of
Dow Corning Toray Silicone Co., Ltd.) 6 parts
Water 37 parts

[0044]

Comparative Example 1

A heat-sensitive recording sheet was obtained in

the same manner as in Example 1 except that potassium myristyl phosphate was not used in the preparation of an outer coating layer coating composition for gloss layer.

Comparative Example 2

A heat-sensitive recording sheet was obtained in the same manner as in Example 1 except that, in place of potassium myristyl phosphate, potassium lauryl phosphate of the same amount was used in the preparation of an outer coating layer coating composition for gloss layer.

Comparative Example 3

A heat-sensitive recording sheet was obtained in the same manner as in Example 1 except that 6 parts of polysiloxane was used as a lubricant in place of potassium myristyl phosphate in the preparation of an outer coating layer coating composition for gloss layer.

[0045]

The heat-sensitive recording sheets obtained in Examples 1 to 5 and Comparative Examples 1 to 3, having a width of 110 mm, were moisture-conditioned for 2 hours under the environmental condition of 20°C and RH 65%, and then subjected to a recording operation using a thermal printer (available under the trade name of "UP-860", from Sony Corporation). Image quality, recording problems and improper operations [sic].

[0046]

(1) Image quality

Each of the five recorded heat-sensitive recording sheets were visually inspected for distinctness, contrast and density irregularity in the image, and rated on the following criteria. o: Good; o~Δ : Fairly good; Δ: Neither good nor bad, Δ~×; Fairly bad; ×: Bad.

(2) Recording problems

Each of the five recorded heat-sensitive recording sheets were visually inspected in terms of recording problems resulting from the running trace of the thermal recording head or the grinding debris adhered to the same, and rated on the following criteria. o: Good; o~Δ : Fairly good; Δ: Neither good nor bad, Δ~×; Fairly bad; ×: Bad.

(3) Improper advance of the recording sheet

Each of the five recorded heat-sensitive recording sheets were visually inspected in terms of duration of operation and recording irregularities with horizontal stripes, and rated on the following criteria. o: Good; o~Δ : Fairly good; Δ: Neither good nor bad, Δ~×; Fairly bad; ×: Bad.

[0047]

As is evident from the results shown in Table 1, the heat-sensitive recording sheets of Examples 1 to 5 showed excellent performance in both image quality and

recording characteristics even under high humidity environmental conditions, whereas the heat-sensitive recording sheets of Comparative Examples 1 to 3 showed in some respects lower performance than those of Examples 1 to 5, the degrees of which varied depending on the sheet.

[Table 1]

No.	Glossiness (%)	Image clarity (%)	Image quality	Recording problems	Improper advance of the recording sheet
Ex. 1	93	94	o	o	o
Ex. 2	92	94	o	o	o
Ex. 3	93	94	o	o	o
Ex. 4	91	95	o	o	o
Ex. 5	92	95	o	o	o
Comp. Ex. 1	93	94	o	×	×
Comp. Ex. 2	92	94	o	×	×
Comp. Ex. 3	92	94	o	×	×

[Effects of the Invention]

As is evident from Table 1 above, the heat-sensitive recording sheet of the present invention provides recorded images that are excellent in image quality, glossiness and image clarity, as well as

excellent recording characteristics, and thus is very useful in practical applications.